

Amperometric Detection of Dissolved Methanol Using Microelectrodes

S. Papadimitriou, A. D. Jiannakoudakis, and S. Sotiropoulos*

Department of Chemistry, Faculty of Sciences,
Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

Abstract: We report on the development of a simple amperometric method for monitoring of dissolved methanol in 0.5 M – 5 M solutions in sulfuric acid (relevant to methanol levels in the feed of direct methanol fuel cells) using bare Pt microdisc electrodes. The high mass transport rates of electroactive species to the microdisc from the solution phase results in a shift of the dissolved oxygen reduction wave to more negative potentials so that it does not interfere with the main methanol oxidation peak at sufficiently positive potentials (+0.5 - +0.7 V vs. Ag/AgCl). For continuous monitoring of methanol a potential sequence consisting of +1.6 V for 10s (cleaning pulse) / 0 V for 120 s (equilibration pulse) / +0.6 V for 180 s (measurement pulse) is applied to the indicator electrode, resulting in current-time transients that are reproducible upon periodic application for at least 8 h. There is a square root correlation between the oxidation current at +0.6 V and methanol concentration for the dissolved methanol sensor in the 0.5–3 M range, in accordance with theoretical predictions, thus excluding electrode poisoning/current saturation up to 3 M. The detection limit was estimated as 0.19 M making this simple method applicable for rough estimates and a crude monitoring of methanol levels.

Keywords: Methanol sensor; Microelectrodes; Amperometric detection.

* To whom correspondence should be addressed.

E-mail: eczss@chem.auth.gr ; Tel.: ++30-2310-997742

Introduction

The determination of dissolved methanol in a wide concentration range (from 10^{-5} M to few M, depending on the application) is essential for a variety of cases ranging from plant, foodstuff and drug analysis to monitoring industrial-process streams and fuel cell feeds [1].

Examples of analytical methods for dissolved methanol determination include spectrophotometry with a detection limit of 10^{-3} M [2], fluorimetry (where methanol is derivatised) with an even higher detection limit [3], GC/MS with a detection limit of 10^{-5} M and an alcohol oxidase-peroxidase amperometric biosensor with detection limit down to 10^{-5} M [4]. Despite the thorough investigations of methanol electro-oxidation as a potential fuel [5, 6] and that practical operation of a fuel cell requires accurate monitoring and control of methanol concentration in the rather high 0.1-2.0 M range, few amperometric sensors for dissolved methanol have been developed. An amperometric Nafion[®]-based Pt sensor of a sandwich-type arrangement has appeared for the concentration range of 0.5 – 3 M [7] whereas a similar sensor with improved characteristics for methanol determination in the anode compartment of a fuel cell has also been proposed [8]. There are no bare electrode or microelectrode sensors for monitoring of dissolved methanol, presumably due to the electrode poisoning and non-linear response.

The aim of this work has been the development of a simple amperometric method for crude monitoring of dissolved methanol in 0.1 M – 3 M solutions in sulfuric acid, relevant to methanol levels in the feed of methanol fuel cells. Its objectives have been: *(i)* the use of bare Pt microdisc indicator electrodes for methanol determination in the presence of oxygen, taking advantage of the high mass transport rates of the interfering dissolved oxygen to decouple the methanol oxidation (which is under pure kinetic control) from oxygen reduction (being under mixed kinetic-mass transfer control), *(ii)* the development of an appropriate potential pulse protocol so that a reproducible amperometric response for methanol oxidation is obtained and *(iii)* the establishment of a calibration curve, a dynamic range and a detection limit for amperometric determination of methanol.

Experimental

Chemicals and Apparatus

The analyte of interest, MeOH, was from Riedel (Chromasolv[®], for HPLC, gradient grade, $\geq 99.9\%$) and solutions were prepared with double-distilled water.

A laboratory made potentiostat with a 1-pA sensitivity and a waveform generator was used, interfaced to a PC with a Duo 18 (WPI, Inc.) AD converter data acquisition system. A small one-compartment cell was the electrochemical test cell.

Electrodes

The Pt microdisc electrodes were prepared by sealing the corresponding Pt microwires (50 μm diameter; Goodfellow Ltd, UK) into borosilicate capillary tubes (WPI Inc., USA) with a two-component epoxy resin glue (RS Components, UK). Thorough polishing of the assembly on emery polishing paper in a direction vertical to its axis removed the excess glue from the tip and revealed a microelectrode disc. The microdisc radius was confirmed to be within 5% of its nominal value by the reversible reduction of ferricyanide from its 5mM solution in 0.1 M NaOH.

An Ag/AgCl electrode (containing 3M KCl as the inner electrolyte, BAS Inc., USA) as the reference electrode and a Pt coil (1 mm diameter wire, Goodfellow Ltd, UK) used as the auxiliary electrode completed the cell.

Results and Discussion

Fig.1(A) presents a cyclic voltammogram (at 2 mV/s) recorded in an air-equilibrated 2 M methanol + 3 M H_2SO_4 solution at a Pt 50 μm diameter microelectrode, together with the background voltammogram of air-equilibrated 3 M H_2SO_4 . It can be seen that the positive-going scan shows the typical methanol oxidation picture with a bell-shaped peak at ca. +0.7 V vs. Ag/AgCl (corresponding to oxidation on a Pt surface covered by surface oxides, whereby the current is rising at low oxide coverage but decreases upon full monolayer formation) and two overlapping voltammetric waves at more positive potentials (corresponding to complete oxidation to CO_2 at a full oxide monolayer and/or multilayers) [9, 10].

The background reduction current, observed at potentials less positive than +0.6 V, is attributed to the reduction of Pt oxides formed when the electrode is exposed to very positive potentials (since it does not disappear completely upon de-aeration and decreases upon lowering the anodic potential limit) and to dissolved oxygen reduction. This background voltammogram, does not interfere with the methanol oxidation peak at +0.7 V vs. SCE, allowing methanol determination at these potentials without the need for oxygen background correction. The latter only affects the methanol oxidation picture during the reverse, negative-going potential scan, suppressing the peak usually observed on an oxide-free Pt surface; this is clearly seen in Fig.1(B) where the background-corrected voltammogram becomes identical to those observed at Pt macro-electrodes in deaerated solutions [9, 10].

In electrochemistry, oxygen is known to interfere with methanol on Pt-electrode in acidic media since the onset potential of its reduction coincides with the onset potential for methanol oxidation [11]. Since its oxidation is known to be always under kinetic control and thus not affected by an increase in the mass transfer rates, the mixed control region of oxygen reduction is expected to shift towards more negative potentials under the high mass transfer at the microdisc, resulting in a favourable separation of these two processes (at least, with respect to the forward methanol oxidation peak).

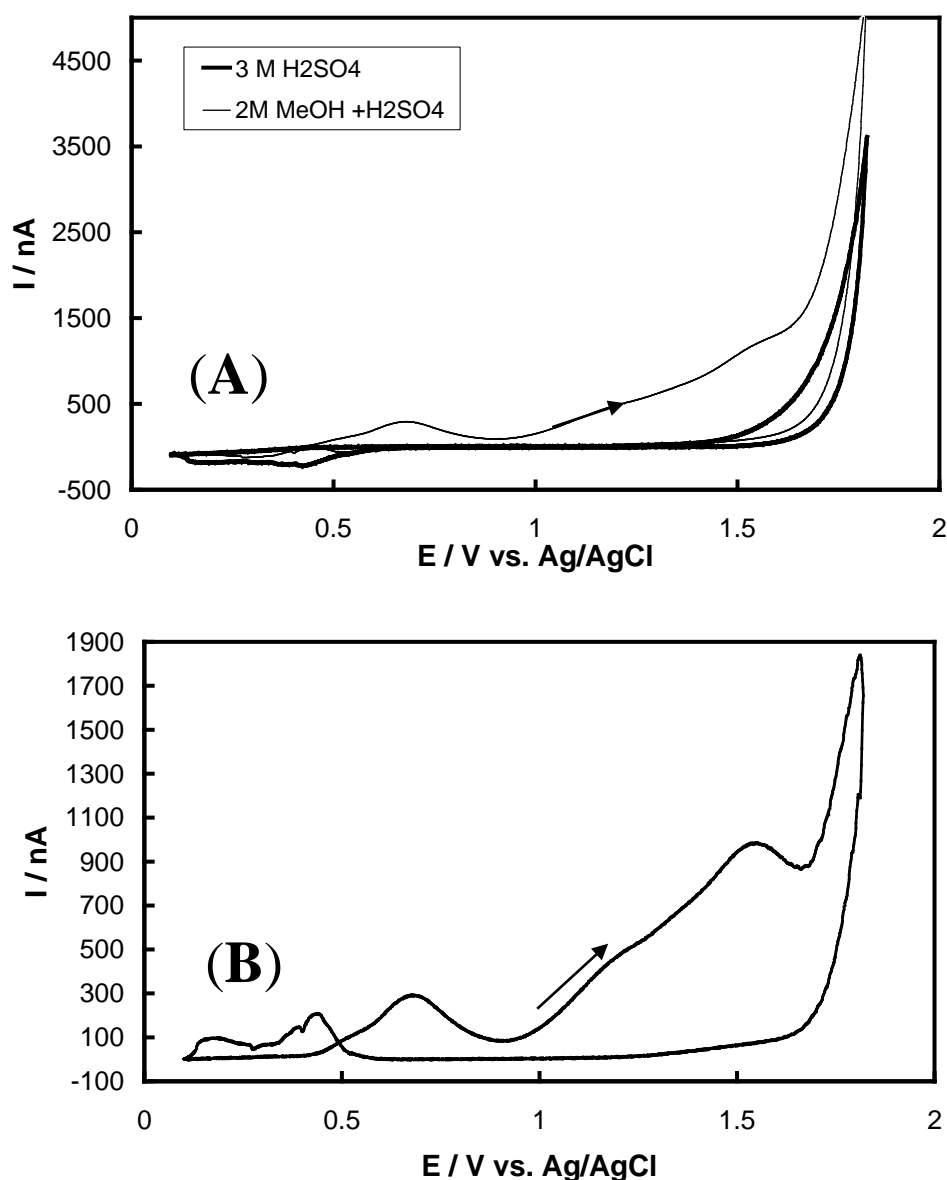


Figure 1: Voltammograms (at 2 mV/s) on a 50 μm Pt-microelectrode, (A) in a 2 M MeOH + 3 M H_2SO_4 air-saturated solution and (B) the previous voltammogram after background (air-saturated 3 M H_2SO_4) correction / subtraction. *Note:* The arrows indicate the potential direction.

Whereas the following Fig. 2 presents voltammograms for two different concentrations of MeOH, Fig.3 shows the variation of the three oxidation peak currents with concentration. It is seen that there is no linear current-concentration dependence and, moreover, at concentrations above 2 M the current starts to drop; possibly, due to increased electrode poisoning by the formation of the poisonous CO intermediate at high methanol concentrations.

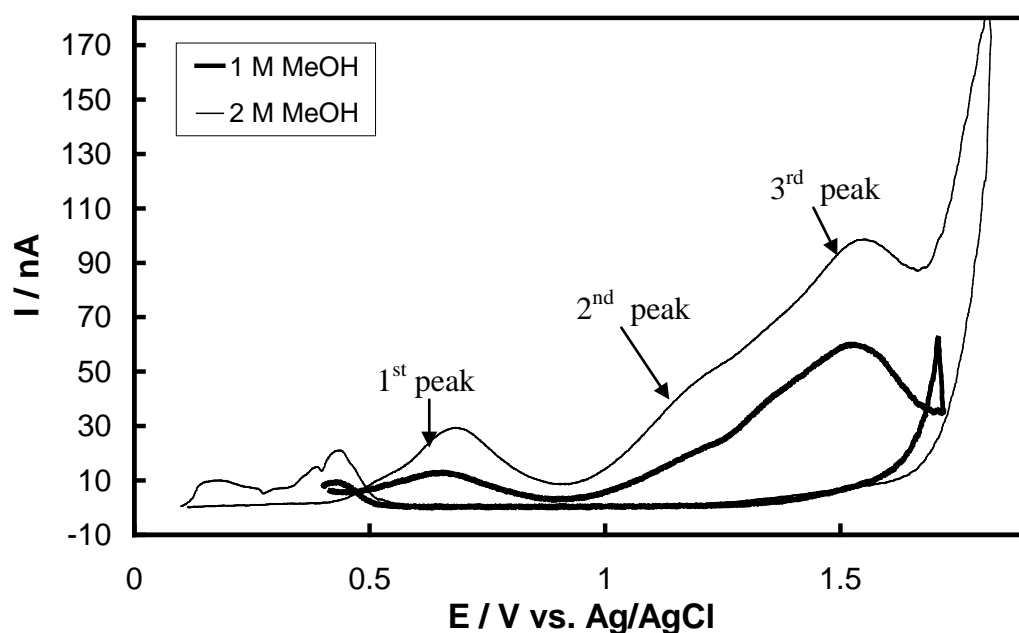


Figure 2. Background-corrected voltammograms on a 50 μm Pt- microelectrode recorded at 2 mV/s in 1M and 2M MeOH + 3M H₂SO₄ air-saturated solutions.

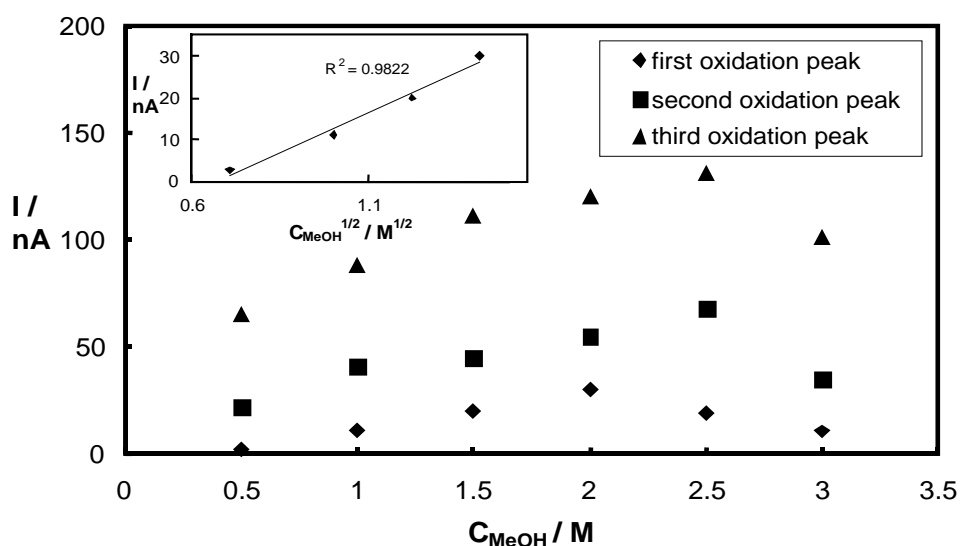


Figure 3: Variation of voltammogram oxidation peak currents with dissolved methanol concentration on a 50 μm Pt microelectrode **Inset:** First peak current vs. the square root of methanol concentration.

The variation of peak current with the square root of methanol concentration up to 2M (Inset to Fig.3) exhibits reasonable linearity, in accordance with the literature which reports a 0.5 reaction order with respect to methanol concentration from aqueous solutions when no severe poisoning takes place [12].

The oxidation rate of methanol on a clean platinum anode is initially large but decays quickly due to partial oxidation products, which build up on the surface and eventually poison the electrode. In their experiments Pletcher and Solis [10] used cycling or pulsing of the electrode through the potential range where platinum oxide is formed to activate the platinum surface. Fedkiw et al [13] introduced a pulsed potential measurement of methanol oxidation, which on average increased the currents by nearly two orders of magnitude above the steady-state current of the same potential. To avoid current deterioration during the continuous monitoring at constant potential and to improve the linearity of the current vs. $C^{1/2}$ curve, a potential sequence consisting of +1.6 V for 10s (cleaning pulse) / 0 V for 120 s (equilibration pulse) / +0.6 V for 180 s (measurement pulse) was applied to the electrodes. During the cleaning pulse all adsorbed organic intermediates and products should be oxidized and removed from the surface while the onset of oxygen evolution should offer mechanical cleaning too. The equilibration pulse at 0 V is necessary for the stripping-reduction of Pt oxides formed during the cleaning pulse and methanol adsorption on a clean Pt-surface.

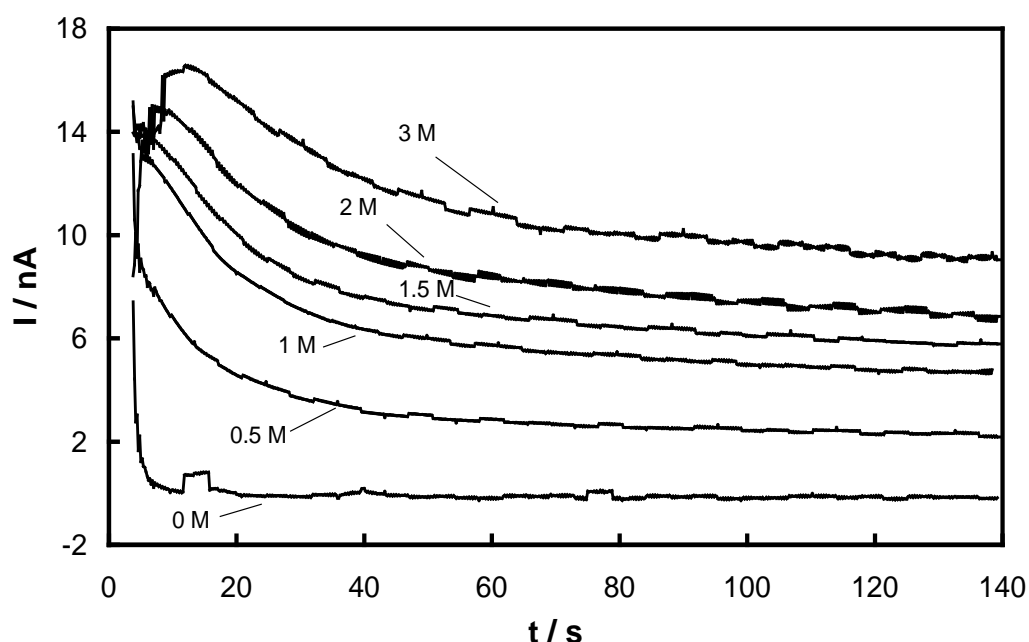


Figure 4: Current / time transients at 50 μm Pt-microelectrode and at the working potential of +0.6 V vs. Ag/AgCl (within the pulse sequence used) in MeOH + 3M H_2SO_4 air-saturated solutions. *Note:* For the individual concentrations, see inscriptions in the figure.

Finally, the measurement pulse was chosen on the potential range of the first oxidation peak which is generally more reproducible and shows a stronger variation with concentration. The resulting current-time transients illustrated in Fig.4 were reproducible upon periodic application of the sequence for at least 8 hours.

The method proved to be sensitive to methanol concentrations above ca. 0.2 M (see below) and thus potentially applicable to crude monitoring of high methanol levels. It should also be noted that an electronic filter of 1 s was employed during the recording of the chronoamperometric transients to cut off oscillations that are known to occur during the potentiostatic and galvanostatic oxidation of organics at high concentrations [14]. The peak of the current transient observed at short times for the higher concentrations studied is similar to that reported by Pletcher and co-workers [10] and can be attributed to the oxidation of methanol pre-adsorbed during the equilibration step following which the current reaches a steady state value corresponding to methanol oxidation from the bulk.

Fig. 5 shows the square root correlations collected at various time intervals between the oxidation current at +0.6 V and methanol concentration that extends from 0.5 M to 3 M. A good linearity is observed in all the measurements ($r^2 > 0.99$; indicating that the pulse protocol helps extend the dynamic range to 3 M) and a steady state response is acquired for times longer than 100 s.

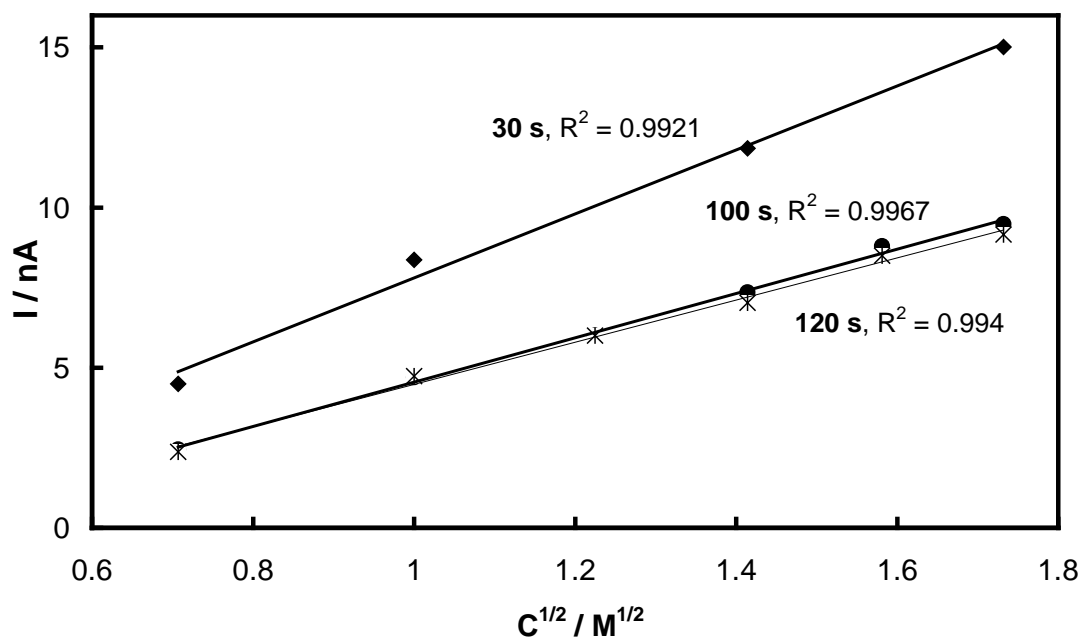


Figure 5. Variation of current collected at various time intervals vs. the square root of methanol concentration.

Since under this protocol, no signal deterioration occurs up to the concentration of 3 M and the corresponding "I vs. C" plot shown in Fig. 6 can be used as a calibration curve and a polynomial fitted to it. Based on this working curve a detection limit of 0.19 M can be estimated (corresponding to a signal of $3I_{(c=0)}$) and a sensitivity of 4.2 nA M^{-1} ($216 \mu\text{A cm}^{-2} \text{ M}^{-1}$) calculated at the 0.5 M methanol concentration level.

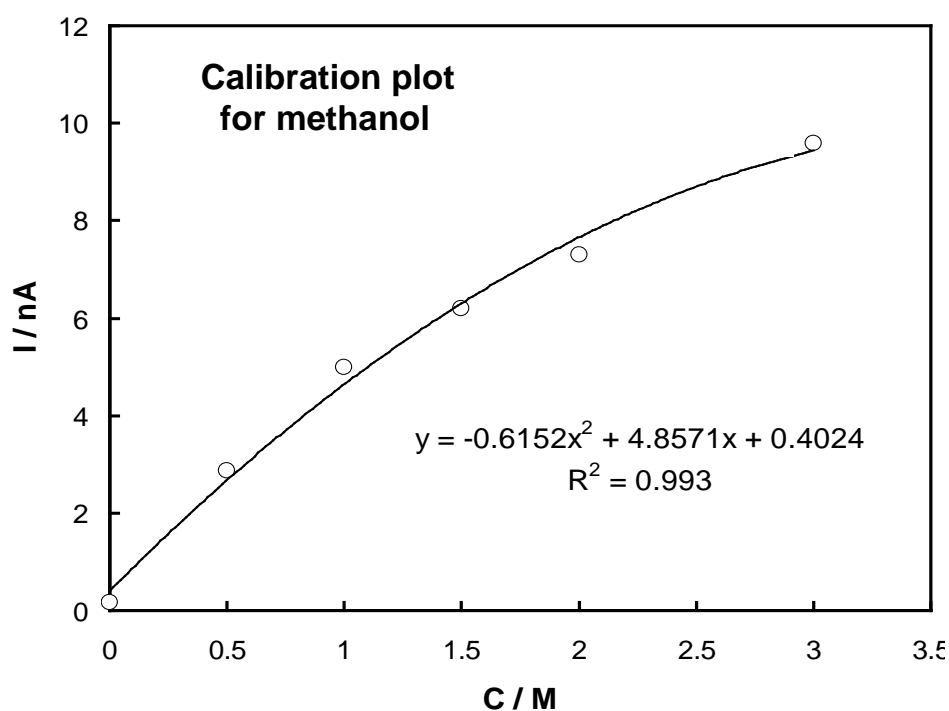


Figure 6. Calibration curve for methanol at a Pt-microelectrode based on the current collected after 120 s at +0.6 V vs. Ag/AgCl, following the pulse amperometric detection of various methanol concentration values, when using a protocol mentioned in the text.

Conclusions

Pt-microelectrodes showed methanol oxidation voltammetry similar to that reported for the macro-variants from the same electrode material, but with a better separation of methanol oxidation and oxygen reduction curves in methanolic solutions containing oxygen, making thus the background recording and subtraction unnecessary.

With a help of an appropriate potential protocol, the amperometric response of the bare Pt-microelectrodes have correlated well with methanol bulk oxidation in the 0.5-3.0 M concentration range, offering a detection limit of about 0.20 M (relevant to methanol fuel cell feed monitoring and control).

References

1. H. H.Kung, W. H.Cheng: *Am. Chem Soc., Division of Petroleum Chem., Preprints* **27** (1982) 597.
2. T. J. Mangos, M. J. Haas: *J. Agric. Food Chem.* **44** (1996) 2977.
3. C. L. Wojciechowski, R. Fall: *Anal. Biochem.* **237** (1996) 103.
4. T. Hasunuma, S. Kuwabata, E. Fukusaki, A. Kobayashi: *Anal. Chem.* **76** (2004) 1500.
5. C. Lamy, J.-M.Léger, S. Srinivasan, in: *Modern Aspects of Electrochemistry* (J. O. M. Bockris, B. E. Conway; Eds.);, Vol. 34, Ch. 3, p. 53. Plenum Press, N.Y. (2000).
6. A.Hamnett, in: *Handbook of Fuel Cells: Fundamentals Technology and Applications*, (W. Vielstich, A. Lamm, H. A. Gasteiger; Eds.), Vol. 1, Ch. 18, p. 305. Wiley, Chichester, (2003).
7. S. A. C. Barton, B. L. Murach, T. F. Fuller, A. C. West: *J. Electrochem. Soc.* **145** (1998) 3783.
8. S. R. Narayanan, T. I. Valdex, W. Chun: *Electrochem. Solid-State Lett.* **3** (2000) 117 120.
9. W.-S. Li, L.-P. Tian, Q.-M. Huang, H. Li, H.-Y. Chen, X.-P. Lian: *Journal of Power Sources* **104** (2002) 281.
10. D. Pletcher, V. Solis: *Electrochim. Acta* **27** (1982) 775.
11. D. Chu, S. Gilman: *J. Electrochem. Soc.* **141** (1994) 168.
12. V. S. Bagotzky, Y. B. Vassilyev: *Electrochim. Acta* **12** (1967) 1323.
13. P. S. Fedkiw, C. L. Traynelis, S.-R. Wang: *J. Electrochem. Soc.* **135** (1988) 2459.
14. W. Vielstich, V. A. Paganin, F. H. B. Lima, E. A.Ticianelli: *J. Electrochem. Soc.* **148** (2001) A502.